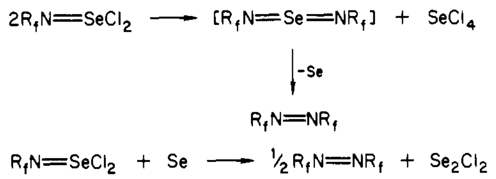
Scheme II



mmol) were reacted under the same conditions given in method A for $CF_3N{=}SeCl_2$. The product $C_2F_5N{=}SeCl_2$ (1.8i g, 6.8 mmol) was isolated as a clear, pale yellow liquid in 76% yield. IR (gas) 1233 (vs), 1212 (vs), 1134 (s), 1097 (vs), 929 (m), 754 (w), 704 (m) cm^{-1}; IR (liquid) 1203 (vs b), 1116 (m), 1084 (s), 933 (m), 753 (w), 704 (m) cm^{-1}; Raman (liquid) 933 (3), 755 (26), 704 (3), 373 (100), 367 (66), 360 (74), 331 (53), 314 (44), 265 (10), 168 (53), 142 (35) cm^{-1}; mass spectrum (70 eV) m/z (relative intensity) 248 $[M - Cl]^+$ (61), 229 $[M - Cl - F]^+$ (35), 214 $[M - CF_3]^+$ (46), 213 $C_2F_5NSe^+$ (23), 194 $C_2F_4NSe^+$ (29), 179 $[M - CF_3 - Cl]^+$ (27), 150 $SeCl_2^+$ (23), 115 $SeCl^+$ (100), 94 NSe^+ (20), 80 Se^+ (34), 69 CF_3^+ (71), 50 CF_2^+ (7); chemical ionization mass spectrum (methane) m/z (relative intensity) 284 $[M + H]^+$ (100), 264 $[M - F]^+$ (71), 248 $[M - Cl]^+$ (65), 214 $[M - CF_3]^+$ (20); ^{19}F NMR δ −86.1 (s, CF_3), −89.5 (s, CF_2); ^{77}Se NMR δ 1088 (t, N=Se, $^3J_{Se-F} = 36.7$ Hz).

Decomposition of $C_2F_5N{=}SeCl_2$. The pentafluoroethyl derivative was found to decompose in a fashion similar to that of $CF_3N{=}SeCl_2$. Analysis by Raman spectroscopy revealed that the white solid formed in the decomposition was $SeCl_4$.[11] A sample of $C_2F_5N{=}SeCl_2$ (1.90 g, 7.0 mmol) left standing in an FEP tube reactor for 4 days gave $C_2F_5N{=}NC_2F_5$[12] (0.53 g, 2.0 mmol) as the principal, volatile, decomposition product. A small quantity of CF_3CN (<0.25 mmol) was also found in the product mixture.

Results and Discussion

The reaction of BrCN with ClF gives a new, efficient method for producing (trifluoromethyl)dichloramine. Previously the best method of preparing CF_3NCl_2 relied on first preparing $CF_3N{=}SF_2$ and then reacting this material with ClF.[9]

$$BrCN + 6ClF \rightarrow CF_3NCl_2 + 2Cl_2 + BrF_3 \qquad (4)$$

$$SF_4 + (FCN)_3 \xrightarrow[155\ °C]{CsF} CF_3N{=}SF_2 \xrightarrow{2ClF} CF_3NCl_2 \qquad (5)$$

The yield in the BrCN reaction is substantially higher, but we have not attempted to scale this reaction beyond 10 mmol.

The dichloramines CF_3NCl_2 and $C_2F_5NCl_2$ react readily with Se_2Cl_2 to give the corresponding iminoselenyl dichlorides and $SeCl_4$.

$$3R_fNCl_2 + 2Se_2Cl_2 \xrightarrow{CCl_3F} 3R_fN{=}SeCl_2 + SeCl_4 \qquad (6)$$

Both reactions proceed at a somewhat higher temperature than does that of the sulfur analogue $SF_5N{=}SeCl_2$ and without the intermediate blackening (elemental Se?).[4] The trifluoromethyl derivative is also formed in the reaction of CF_3NCl_2 with elemental selenium; however, one cannot rule out the initial formation of Se_2Cl_2 in this reaction.

$$CF_3NCl_2 + Se \rightarrow CF_3N{=}SeCl_2 \qquad (7)$$

Diselenium dichloride was also found to react with $FC(O)NCl_2$, but the reaction product was too unstable to be isolated and characterized.

The instability of the (perfluoroalkylimino)selenyl halides is not totally unexpected. It is surprising that the major products of the decomposition are not analogous to those observed in the decomposition of $SF_5N{=}SeCl_2$.[4] Only a small quantity of CF_3CN observed in the decomposition of $C_2F_5N{=}SeCl_2$ gave evidence for an analogous pathway.

$$2SF_5N{=}SeCl_2 \rightarrow 2SF_3{\equiv}N + SeCl_4 + SeF_4 \qquad (8)$$

$$2C_2F_5N{=}SeCl_2 \rightarrow 2CF_3C{\equiv}N + SeCl_4 + SeF_4 \qquad (9)$$

Other evidence indicates that the major decomposition reaction is that shown in eq 10. A possible mechanism for this decomposition is shown in Scheme II. This mechanism is supported by the early appearance of $SeCl_4$ in the decomposition and by the fact that both $CF_3N{=}SeCl_2$ and $C_2F_5N{=}SeCl_2$ react with elemental selenium to give the respective perfluoroazoalkane and a heavy, red liquid believed to be Se_2Cl_2. Sharpless and co-workers have also previously proposed selenium diimides as reactive intermediates in organic syntheses.[13]

$$6R_fN{=}SeCl_2 \rightarrow 3R_fN{=}NR_f + 2SeCl_4 + 2Se_2Cl_2 \qquad (10)$$

The Raman stretching frequencies at 1028.5 cm^{-1} in $CF_3N{=}SeCl_2$ and at 933 cm^{-1} in $C_2F_5N{=}SeCl_2$ have been assigned to the N=Se stretch. A similar, unexpectedly large difference in the N=Se stretching frequencies of $SF_5N{=}SeCl_2$ and $TeF_5N{=}SeCl_2$ (~80 cm^{-1}) has previously been observed.[4] A possible explanation for this variation could be the degree of association and/or association mechanism in these compounds.[14] The selenium-77 NMR spectra reported herein are consistent with Se(IV) species, and the observed couplings to fluorine strongly support the identity of the new compounds.

Acknowledgment. Financial support of this research by the U.S. Army Research Office (Grant DAAG 29-83-K6173) and the National Science Foundation (Grant CHE-8217217) is gratefully acknowledged.

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Nephelauxetic Effect in Metal Ion Paramagnetic Shielding of Spin-Paired d^6 Transition-Metal Complexes

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Electronic configuration of the spin-paired $3d^6$, $4d^6$, and $5d^6$ transition-metal complexes is properly described by the strong-field ligand field scheme, as has been well documented in the study of their electronic absorption spectra.[1] Therefore, magnetic shielding of metal ions in such complexes may be evaluated by the same general approach of Griffith and Orgel[2] that has been first applied to the cobalt(III) complexes.[3] Thus, magnetic shielding in all spin-paired d^6 complexes is expected to be dominated by the large paramagnetic shielding term arising through mixing of the excited $^1T_{1g}(t_{2g}{}^5e_g)$ state with the ground $^1A_{1g}(t_{2g}{}^6)$ state. This term is also strongly influenced by ligands (unlike the diamagnetic shielding term) and contains valuable information about metal–ligand bond covalency.[4,5] The effect of covalency has been conveniently quantified by introduction of the circulation removing ratio (η), which allows the paramagnetic shielding term (σ^P) to be expressed as[6]

$$\sigma^P = -\frac{\mu_0}{4\pi}(32\mu_B{}^2)\langle r^{-3}\rangle_{d_F}\frac{\eta}{\Delta E} \qquad (1)$$

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Table I. Magnetogyric Ratio of Unshielded Metal Nucleus (γ_0), Reference Magnetogyric Ratio (γ_s), Free-Atom Diamagnetic Shielding Constant (σ^d), and Free-Ion Expectation Value of d-Electron Inverse Cube Distance ($\langle r^{-3}\rangle_{d_F}$) for Transition Metals Considered

	γ_0, MHz T^{-1}	ref	γ_s,[a] MHz T^{-1}	ref	σ^d [20]	$\langle r^{-3}\rangle_{d_F}$,[b] au	ref
^{51}V	11.143	9[c]	11.198 ($VOCl_3$)	14	0.0017	2.08	9
^{57}Fe	1.376	10[d]	1.3785 ($Fe(CO)_5$)	15	0.0021	5.08	17
^{59}Co	10.057	11[e]	10.1029 ($Na_3Co(CN)_6$)	3[h]	0.0022	6.65	17
^{103}Rh	1.343	12[f]	1.3453 (13.6 MHz)[g]	16	0.0044	7.0	12, 18
^{195}Pt	9.174	13[f]	9.1111 (21.4 MHz)[g]	16	0.0094	10	19

[a] This is the ratio for the standard reference given in parentheses. [b] Values for the free-ion d^6 configuration. For Rh^{3+} and Pt^{4+} approximate values are estimated from data on the lower oxidation states. [c] Derived from $\sigma(K_3VO_4) = 4887$ ppm. [d] The value is uncorrected for magnetic shielding, but σ^p is expected to be of the order of σ^d; hence, $\sigma^p + \sigma^d \sim 0$. [e] From the shift anisotropy of $[CoCp_2]ClO_4$, after correction for core-electron diamagntism. [f] After correction for core-electron diamagnetism. [g] In this case the frequency at standard field has been accepted as the reference. [h] From the ratio $\nu(^{59}Co)/\nu(^{23}Na)$.

Table II. Metal Ion Chemical Shifts (δ), Paramagnetic Shieldings (σ^p) Calculated by Eq 2, $^1T_{1g} \leftarrow {}^1A_{1g}$ Electronic Transition Energies (ΔE), and Nephelauxetic Ratio (β_{35}) in Spin-Paired d^6 Transition-Metal Complex Ions

complex ion	δ	σ^p	$\Delta E/10^3$, cm^{-1}	β_{35}	ref[a]
$[V(CO)_6]^-$	−880	0.0058	24.0	(0.67)[b]	21, 22
$[Fe(CN)_6]^{4-}$	2497	0.0064	31.0	0.45	15, 1
$[Co(OH_2)_6]^{3+}$	15100	0.0219	16.5	0.61	23, 1
$[Co(NH_3)_6]^{3+}$	8170	0.0150	21.0	0.56	3, 1
$[Co(CN)_6]^{3-}$	0	0.0068	32.1	0.42	3, 1
$[Rh(OH_2)_6]^{3+}$	9992	0.0161	25.5	0.71	24, 1
$[RhCl_6]^{3-}$	7985	0.0141	19.3	0.48	25, 1
$[RhBr_6]^{3-}$	7077	0.0132	18.1	0.39	25, 1
$[PtF_6]^{2-}$	11847	0.0143	31.5	0.53	16, 1
$[PtCl_6]^{2-}$	4521	0.0070	26.4	0.17	16, 26

[a] First reference is for chemical shift; second, for optical data. [b] Calculated by using an estimated value of $B_0 \sim 650\ cm^{-1}$.

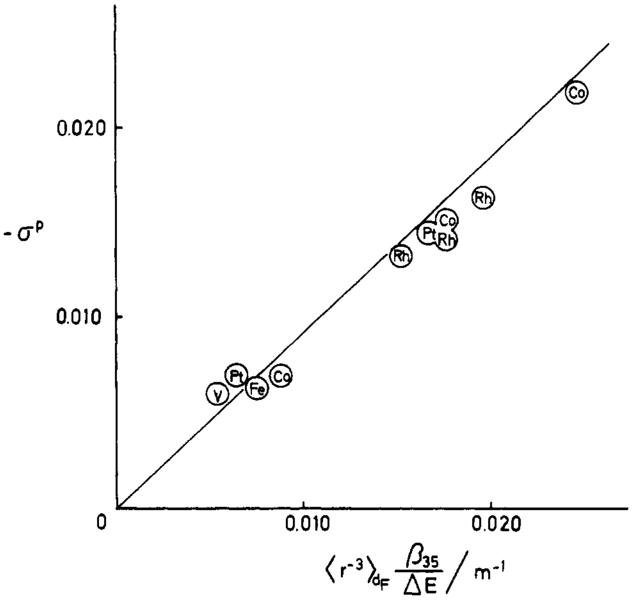

Figure 1. Correlation of paramagnetic shieldings with ligand field parameters according to eq 2. Solid line indicates expected slope. Note that $\langle r^{-3}\rangle_{d_F}$ is in atomic units.

(μ_B is the Bohr magneton, $\langle r^{-3}\rangle_{d_F}$ is the free-ion expectation value of the d-electron inverse cube distance, and ΔE is the energy of the $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition). This equation is the basis for a general rationalization of σ^p values in terms of the nephelauxetic effect. Namely, in the previous work on cobalt(III) complexes[6-8] I have established that the circulation removing ratio has a value close to that of the nephelauxetic ratio, i.e. $\eta \sim \beta_{35}$. Therefore, it may be expected that the approximative relation (2),

$$\sigma^p \sim -\frac{\mu_0}{4\pi}(32\mu_B{}^2)\langle r^{-3}\rangle_{d_F}\frac{\beta_{35}}{\Delta E} \tag{2}$$

obtained when in eq 1 η is replaced by β_{35}, is generally valid for the paramagnetic shielding of metal ions in the spin-paired d^6 complexes. In this work eq 2 is applied to vanadium(−I), iron(II), cobalt(III), rhodium(III), and platinum(IV) complexes.

Paramagnetic shielding term values may be extracted from experimental magnetogyric ratios of metal ions in complexes

$$\gamma = \gamma_0(1 - \sigma^d) - \gamma_0\sigma^p \tag{3}$$

provided that the magnetogyric ratio of the unshielded metal nucleus (γ_0) is known, as well as the metal ion diamagnetic shielding in complexes (σ^d). The latter could be replaced by the diamagnetic shielding constant of the free metal atom, since the core-electron contribution to this shielding is by far the most important. Determination of γ_0 of transition-metal nuclei is a greater problem. It has been approached by different techniques, and the best available values are given in Table I. On the basis of eq 3, the paramagnetic shielding in complexes is now calculated from the expression

$$\sigma^p = [\gamma_0(1 - \sigma^d) - \gamma_s(1 + \delta)]/\gamma_0 \tag{4}$$

where magnetogyric ratios of metal ions in complexes are expressed through metal ion chemical shifts (δ) and the reference magnetogyric ratio (γ_s); i.e., $\gamma = \gamma_s(1 + \delta)$. The reference magnetogyric ratios are given in Table I, while chemical shifts and calculated values of paramagnetic shieldings of complexes considered are presented in Table II. In the view of the uncertainities of the γ_0 values, I estimated that calculated paramagnetic shieldings are reliable to about ±0.0005.

The general correlation of paramagnetic shieldings with ligand field parameters $\langle r^{-3}\rangle_{d_F}\beta_{35}/\Delta E$, which according eq 2 has to be common to all spin-paired d^6 complexes, is presented in Figure

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1. It strongly supports the suggested rationalization of the σ^{p} values, since deviations from the expected slope, $32\ \mu_{\mathrm{B}}^2\mu_0/4\pi$, are within 10%. This finding is highly satisfactory in the sense that it is an independent demonstration of the nephelauxetic effect in transition-metal complexes. In fact, by calculating the circulation removing ratio from paramagnetic shielding on the basis of eq 1, we are able to gain insight into the nephelauxetic effect of complexes for which β_{35} is not known.

Registry No. $[V(CO)_6]^-$, 20644-87-5; $[Fe(CN)_6]^{4-}$, 13408-63-4; $[Co(OH_2)_6]^{3+}$, 15275-05-5; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(CN)_6]^{3-}$, 14897-04-2; $[Rh(OH_2)_6]^{3+}$, 16920-31-3; $[RhCl_6]^{3-}$, 21412-00-0; $[RhBr_6]^{3-}$, 30211-18-8; $[PtF_6]^{2-}$, 16871-53-7; $[PtCl_6]^{2-}$, 16871-54-8.

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Ruthenium(III) Tertiary Amine Complexes

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The chemistry of ruthenium(III) amine complexes has continued to be an active area of research in our laboratories.[1] Though the synthetic chemistry of ruthenium(III) complexes with primary and secondary amines has been well developed, their redox chemistry is usually complicated by oxidative dehydrogenation of the coordinated amines.[2] We have recently found that high-valent ruthenium(IV) and -(VI) oxo species could be prepared from complexes containing saturated tertiary amines.[3,4] Here, the synthesis and characterization of a class of ruthenium(III) complexes containing bidentate and macrocyclic tertiary amines are described. Our findings indicated that these tertiary amines, upon coordination to ruthenium, are particularly stable under drastic oxidizing conditions.

Experimental Section

Materials. $K_2[RuCl_5H_2O]$ (Johnson and Matthey) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) (Strem) were used as supplied. All solvents used were of analytical grade and *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (TMEA) was distilled and stored over KOH before use.

***trans*-[Ru(TMC)Cl$_2$]Y (Y = Cl, ClO$_4$).** The chloride salt was prepared by suspending $K_2[RuCl_5H_2O]$ in absolute ethanol (1 g in 150 cm^3), and the suspension was heated under reflux and with vigorous stirring for about 15 min. An ethanolic solution of TMC (0.8 g in 200 cm^3) was added dropwise to the refluxing suspension, and the process took about 5 h for completion. After being further heated under reflux overnight, the solution was filtered while hot and the filtrate was evaporated to dryness. The residue was then dissolved in a minimum amount of hot HCl (3 mol dm^{-3}). Upon cooling, yellow crystals of *trans*-[Ru(TMC)Cl$_2$]Cl deposited. As *trans*-[Ru(TMC)Cl$_2$]$^+$ has been found to be very substitutionally labile,[5] *trans*-[Ru(TMC)Cl$_2$]ClO$_4$ was obtained by the metathesis of *trans*-[Ru(TMC)Cl$_2$]Cl with NaClO$_4$ in HCl (2 mol dm^{-3}), which helps to suppress the hydrolysis of the Cl$^-$ ligands. Overall yield of the reaction ranges from 20% to 40%. Anal. Calcd for [Ru(TMC)Cl$_2$]ClO$_4$: C, 31.8; H, 6.1; N, 10.6; Cl, 20.2. Found: C, 31.7; H, 6.0; N, 10.3; Cl, 20.2. $E_f°$ (V vs. NHE) = 0.140 in HCl (2 mol dm^{-3}).

***trans*-[Ru(TMEA)$_2$Cl$_2$]Y (Y = Cl, ClO$_4$).** These complexes were prepared by essentially the same method as that described for *trans*-[Ru(TMC)Cl$_2$]ClO$_4$ except that TMEA and methanol were used instead. After the methanolic suspension of $K_2[RuCl_5H_2O]$ was refluxed with TMEA overnight, a bluish green solution was obtained. This was filtered, and the filtrate was evaporated to dryness. The crude solid obtained was dissolved in boiling HCl (2 mol dm^{-3}), filtered, and purified through chromatography on a Sephadex C-25 column with HCl (2 mol dm^{-3}) as the eluent. The first band (yellow) was identified as *trans*-[Ru(TMEA)Cl$_2$]$^+$ by measuring its UV–vis absorption spectrum. The second and third bands were dark blue and red, respectively. No further attempts were made to characterize these species. The first band was collected, and the solution was then rotary evaporated down to ~10 cm^3. On cooling, yellow crystals of *trans*-[Ru(TMEA)Cl$_2$]Cl deposited. The perchlorate salt was obtained by the metathesis of *trans*-[Ru(TMEA)Cl$_2$]Cl with NaClO$_4$ in HCl (2 mol dm^{-3}). Overall yield of the reaction ranges from 20% to 30%. Anal. Calcd for [Ru(TMEA)Cl$_2$]ClO$_4$: C, 28.6; H, 6.3; N, 11.1; Cl, 21.2. Found: C, 28.7; H, 6.0; N, 11.0; Cl, 21.4. $E_f°$ (V vs. NHE) = 0.14 in NaClO$_4$ solution (0.1 mol dm^{-3}).

Table I. Infrared Spectra in the Regions 3500–1300 and 100–600 cm^{-1} of Ruthenium(III) Tertiary Amine Complexes[a]

complex	absorption bands, cm^{-1}
trans-[Ru(TMC)Cl$_2$]ClO$_4$	990 (m), 970 (w), 960 (s), 945 (w), 910–920 (br, m), 840 (m), 830 (m), 810 (m), 790 (m), 750 (br, m), 720 (w)
trans-[Ru(TMC)(NCO)$_2$]ClO$_4$	3520 (m), 2240 (vs, br),[b] 1340 (s),[b] 990 (m), 970 (w), 960 (s), 945 (w), 925 (w), 916 (m), 840 (m), 830 (m), 810 (m), 790 (m), 750 (m), 720 (w)
trans-[Ru(TMC)(NCS)$_2$]ClO$_4$	2020 (vs, br),[c] 985 (m), 970 (w), 960 (s), 940 (w), 915 (m), 860 (w), 840 (m), 810 (m), 790 (m), 750 (m), 740 (w), 720 (w)
trans-[Ru(TMC)(NCS)Cl]ClO$_4$	2020 (vs, br),[c] 985 (m), 960 (br, s), 940 (w), 915 (br, w), 845 (m), 810 (m), 790 (m), 720 (w)
trans-[Ru(TMEA)$_2$Cl$_2$]ClO$_4$	946 (s), 915 (w), 800 (m), 770 (m)

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad. [b] ν_{as}(NCO) = 1340 cm^{-1}, ν_{s}(NCO) = 2240 cm^{-1}. [c] ν(C≡N) = 2020 cm^{-1}.

***trans*-[Ru(TMC)(NCS)$_2$]Y (Y = NCS, ClO$_4$).** This was prepared by heating an aqueous solution (50 cm^3) of *trans*-[Ru(TMC)Cl$_2$]Cl (0.4 g) and NaNCS (4 g) on a steam bath for $^1/_2$ h. A blue-violet crystalline solid of *trans*-[Ru(TMC)(NCS)$_2$]NCS came out on cooling. *trans*-[Ru(TMC)(NCS)$_2$]ClO$_4$ was obtained by metathesis of *trans*-[Ru(TMC)(NCS)$_2$]NCS with NaClO$_4$ in water; overall yield >70%. Anal. Calcd for [Ru(TMC)(NCS)$_2$]NCS: C, 38.4; H, 6.0; N, 18.4; S, 18.1. Found: C, 38.5; H, 6.2; N, 18.2; S, 18.4. IR: ν(C≡N) 2020 cm^{-1} (Nujol mull). $E_f°$ (V vs. NHE) = 0.42 in HClO$_4$ (0.1 mol dm^{-3}).

***trans*-[Ru(TMC)(NCS)Cl]Y (Y = PF$_6$, ClO$_4$).** This was prepared by heating an ethanolic solution of *trans*-[Ru(TMC)Cl$_2$]Cl (0.3 g in 50 cm^3) and NaNCS (2 g) on a steam bath. The course of the reaction was followed by monitoring the UV–vis spectral changes. When the peak at 370 nm disappeared and the peak at ~520 nm developed,[6] excess LiClO$_4$ was added to the solution mixture. The violet-red precipitate obtained was filtered off and was purified by chromatography on a Sephadex C-25 column with HCl (0.1 mol dm^{-3}) as the eluent. Three bands were observed. The first and the last band were *trans*-[Ru(TMC)(NCS)$_2$]$^+$ and *trans*-[Ru(TMC)Cl$_2$]$^+$, respectively, whereas the middle one (major portion) was *trans*-[Ru(TMC)(NCS)Cl]$^+$. The middle portion was preconcentrated down to ~15 cm^3, and upon addition of NaClO$_4$, *trans*-[Ru(TMC)(NCS)Cl]ClO$_4$ was precipitated out. This was purified by rechromatography on a Sephadex C-25 column; yield ~60%. The PF$_6^-$ salt was obtained by metathesis of *trans*-[Ru(TMC)(NCS)Cl]ClO$_4$ and NaPF$_6$ in HCl (0.1 mol dm^{-3}). Anal. Calcd for [Ru(TMC)(NCS)Cl]PF$_6$: C, 30.2; H, 5.4; N, 11.8; Cl, 6.0. Found: C, 30.1; H, 5.4; N, 11.9; Cl, 6.2. IR: ν(C≡N) 2020 cm^{-1} (Nujol mull). $E_f°$ (V vs. NHE) = 0.24 in HClO$_4$ (0.1 mol dm^{-3}).

***trans*-[Ru(TMC)(NCO)$_2$]ClO$_4$.** *trans*-[Ru(TMC)(NCS)$_2$]NCS (0.4 g) and 30% H$_2$O$_2$ (2 cm^3) in H$_2$O (50 ml) was heated on a steam bath with continuous stirring. When the color of the solution changed from blue to yellow, the solution was ice cooled and filtered, if necessary. Upon addition of excess NaClO$_4$, yellow solid of *trans*-[Ru(TMC)(NCO)$_2$]ClO$_4$ was precipitated out. This was filtered off, washed with ice-cooled water, and dried under vacuum at room temperature; overall yield >70%. Anal. Calcd for [Ru(TMC)(NCO)$_2$]ClO$_4$: C, 35.5; H, 5.9; N, 15.5; Cl,

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